# Examination of precipitation chemistry and improvements in precision using the $Mg(OH)_2$ preconcentration ICP-MS method for high-throughput analysis of open-ocean Fe and Mn in seawater

Mak A. Saito[1*] and David L. Schneider[1,2]

[1] Marine Chemistry and Geochemistry Department
Woods Hole Oceanographic Institution
Woods Hole MA 02543
USA

[2] ICP-MS Facility
Woods Hole Oceanographic Institution
Woods Hole MA 02543
USA

*corresponding author, 508-289-2393, mak@whoi.edu

Revised for Analytical Chimica Acta
February 14th, 2006

**Abstract**

The chemistry of magnesium precipitation preconcentration of Fe, Mn and Co from seawater was investigated, and this analytical technique was adapted for use with the Element-2 inductively coupled plasma mass spectrometer (E2 ICP-MS). Experiments revealed that the scavenging efficiency of Mn using the precipitation protocol described here was ~95% and similar to that previously observed with Fe. In contrast, the scavenging efficiency of Co was three-fold lower than that of Fe and Mn, resulting in poor recovery. An increase in sample size to 13mL led to several desired effects: 1) an increase in the Fe and Mn signals allowing a final dilution of samples to 0.5mL and the use of an autosampler, 2) an increase in precision to ~1-2.5% RSD, 3) an increase in signal relative to the blank. Experiments suggest metal concentration from seawater occurs during the formation of $Mg(OH)_2$ precipitate, whereas P was scavenged by adsorption onto the $Mg(OH)_2$ particles. Example vertical profiles are shown for dissolved Fe and Mn from the Equatorial Pacific.

**Keywords:** ICP-MS, iron, manganese, cobalt, magnesium co-precipitation, seawater, $Mg(OH)_2$

## 1. Introduction

In recent decades the importance of trace elements, in particular iron, in controlling primary productivity of the oceans has become clear. The primary productivity in major regions of the oceans is predicted to be directly limited by iron or indirectly by iron limitation of the cyanobacterial nitrogen fixers [1]. However, geographical coverage of iron and other trace metals is quite sparse compared to major nutrients [2, 3]. The difficulty in analytical methods and the potential for inadvertent contamination by metal-laden dust particles has limited the number of high-quality data sets, with studies often consisting of only a few vertical profiles or transects. Early reliable measurements of iron and other trace elements utilized the APDC solvent extraction method for pre-concentration coupled to atomic absorption spectrometry [4-6] or preconcentration with Chelex-100 and atomic adsorption analysis [7, 8]. These methods, while having a high precision and accuracy, require large liter-scale sample volumes and are relatively labor intensive in both sample collection and analysis. More recently, electrochemical, flow-injection analysis with spectrophotometric detection, chemiluminescence, and inductively coupled plasma mass spectrometry (ICP-MS) methodologies have become available [9-16]. Electrochemical analyses have the advantage of being able to also characterize the natural organic ligands that bind iron and other metals in seawater [17-20]; however, these methods tend to be labor intensive, can require long deposition times to achieve good sensitivity with some elements (e.g. Zn and Cd), and can typically only analyze one or two elements at a time. For total dissolved metals, flow injection analysis with spectrophotometric detection and ICP-MS methods offer the potential for adaptation for high-throughput analysis of iron and other trace elements.

The ICP-MS methods currently utilize three approaches: 1) direct injection of small volumes of seawater for coastal seawater samples with high trace metal concentrations [21], 2) preconcentration using metal affinity resins [22-24], and 3) preconcentration using magnesium hydroxide ($Mg(OH)_2$) precipitation [14, 15, 25]. The latter two approaches have the sensitivity needed for open ocean samples, but both methods require detailed studies of the preconcentration chemistries involved to avoid artifacts or problems with accuracy. Recently, further examination of and improvements

in the affinity resin chemistry (#2 above) have showed excellent precision and sensitivity for Fe and Cu, and pointed out complications with Fe(II) affinity and the need for $H_2O_2$ additions to oxidize Fe(II) [22]. The other low level ICP-MS method, the $Mg(OH)_2$ preconcentration technique (#3 above) is a straightforward technique that involves the addition of a base, such as ammonia, resulting in the precipitation of magnesium, which already present in the samples as a major constituent of seawater. The protocol for the method is straightforward: a known volume of seawater sample is spiked with an isotopic spike (e.g. $^{57}Fe$), $Mg(OH)_2$ is precipitated by the addition of base (ammonia), centrifuged to remove the seawater supernatant, and finally redissolved in a small volume of dilute nitric acid for analysis on the ICP-MS. Because the precipitating components are part of the sample matrix (natural Mg in seawater), only a few reagents used in small quantities are required, thus avoiding the need for complex reagent cleanup protocols. Given that both of these low-level ICP-MS techniques may become the ideal methods for future large scale international ocean trace metal measurement programs (i.e the proposed GEOTRACES [26]), improving our understanding of the chemistry behind them is imperative.

The Mg precipitation preconcentration technique has been used in various analytical formats over the years. Early inductively coupled plasma/atomic emission spectrometry (ICP-AES) approaches of this technique utilized the addition of gallium hydroxide to scavenge trace elements from seawater through the co-precipitation with $Mg(OH)_2$ [27]. This method relied on large 1L sample volumes and filtration of the precipitant. The Mg precipitation preconcentration technique has also been applied to measuring low level oceanic dissolved phosphorus [28]. Most recently, this preconcentration technique has been coupled to ICP-MS analysis, allowing the use of isotope dilution methods for quantification of trace metals at small sample sizes [14, 15]. This technique has also begun to be applied to the low level (oceanic) analysis of elements that do not lend themselves to the use of isotope dilution due to the lack of multiple stable isotopes (e.g. Mn [29]).

These recent developments suggest that Mg precipitation method has the promise of becoming a high-sensitivity and high-throughput technique capable of analyzing multiple elements at extremely scarce open ocean seawater abundances. However, the

extension of this technique to multiple elements for simultaneous analysis requires a careful study of the chemistry involved in the pre-concentration step to ensure accuracy and maximize precision. There are methodological details and assumptions that are important in the application of this method, particularly for elements where there is only a single stable isotope and isotope dilution cannot be utilized. These have been discussed to some extent in previous studies [14, 15, 29], and in this manuscript we perform some detailed experiments examining the nature of the Mg precipitation and the resultant implications for these assumptions. We describe four assumptions here: first, the addition of the $^{57}Fe$ spike is important in acting as an internal standard for $Mg(OH)_2$ recovery during decanting steps, thereby correcting for small losses of the precipitate during decanting [29]. While this correction is already taken into account as part of the isotope dilution calculations, the correction is also important in its application to elements with only a single stable isotope where isotope dilution cannot be used. Second, the matrix effects associated with the $Mg(OH)_2$-rich solutions can also be corrected for using an iron isotopic spike [29] and/or indium as an internal standard. Third, the scavenging efficiency, which is basically the effectiveness of the $Mg(OH)_2$ in removing the trace element(s) of interest from the seawater, needs to be quantified on an element-by-element basis if isotope dilution cannot be used. Previous examinations of iron preconcentration have shown a scavenging efficiency of greater than 90% after single precipitations[15]. Fourth, the influence of the quantity of $Mg(OH)_2$ precipitate and the time allowed for the precipitation reaction on recoveries may have an influence on the scavenging efficiencies and matrix effects [15]. In this study, we present laboratory experiments that provide a detailed examination of the Mg precipitation chemistry, focusing on the influence of precipitation time, sequential precipitations, the use of previously precipitated seawater, and exposure of fresh seawater to precipitates on the precision, accuracy, and element-specific recovery. These results are then discussed within the context of the assumptions (listed above) involved in methodology and associated quantification calculations. In addition, an improvement in precision achieved with some minor adjustments is described. Finally, the ICP-MS performance with a desolvator and with X-sample and skimmer cones is described.

## 2. Materials and Methods

### *2.1 Cleaning of Plasticware*

Oceanic samples have the lowest aqueous concentrations of trace elements found in nature. Significant precautions were taken at every step to avoid contamination from a wide variety of sources. All plasticware used in this study was rinsed with Milli-Q water, leached with 10% HCl (Baker Instra-analyzed grade) for one week or 48h at 60$^{o}$C, rinsed three times with dilute ultraclean HCl (Seastar) at pH 2. Sample tubes were also rinsed with sample seawater prior to use. All cleaning and labwork was conducted in a filtered air cleanroom environment that exceeded Class-100 cleanroom specifications.

### *2.2 Sample collection and preservation*

Uncontamined seawater was collected using 10L Teflon coated Go-Flo bottles (General Oceanics) that had been washed with Citranox detergent initially and acid leached. Go-Flo bottles were attached to a non-metallic Kevlar line and a non-metallic metering block. Samples were dispensed from the bottle within a shipboard fabricated cleanroom with HEPA particle filters, filtered through acid-leached 0.4μm polycarbonate filters, and stored in trace metal clean low-density polyethylene (LDPE) bottles. Seawater samples were acidified to a pH of 1.7 with high purity HCl (Seastar Chemicals Inc.) and stored at room temperature for several months to dissolve any metals that had adhered to the bottle walls prior to acidification.

### *2.3 Magnesium-hydroxide preconcentration*

The magnesium precipitation preconcentration protocol is slightly modified from previous published protocols [15, 25, 29] to allow increases in precision as well as the use of an autosampler on the ICP-MS. Trace metal clean 15mL polypropylene centrifuge tubes (Globe Scientific Inc.) are utilized for the precipitation reaction as opposed to previous studies utilizing 1.3mL samples in microcentrifuge tubes. The seawater sample was added to the tubes to a volume of 13.0mL and allowed to equilibrate with a $^{57}$Fe spike overnight (~0.75nM). The precipitation protocol involves the addition of a small amount of high-purity ammonium hydroxide (Seastar Chemicals Inc.) to the sample resulting in the precipitation of the Mg present in seawater as $Mg(OH)_2$, and the resultant

preconcentration of trace metals with the $Mg(OH)_2$. After allowing 90s of $Mg(OH)_2$ precipitation to occur without disturbance, the sample is inverted 6 times to mix the precipitate throughout the sample. After an additional 180s the sample is centrifuged at 3000rpm (1460g) for 3min at room temperature (Brinkmann 5810 swinging bucket). The sample is then decanted and recentrifuged at 3000rpm for 3min, followed by an additional decanting. For analyses using a single seawater precipitation, the pellet was redissolved in 500µl of 5% nitric acid with trace quantities of indium added (Seastar Chemicals Inc., and Element-grade Milli-Q water) and transferred to a cleaned autosampler tube. In some samples, second precipitations were performed to reduce the Mg in the sample. In these samples 50µl of 5% nitric acid was used to redissolve the pellet, followed by the addition of 0.65mL of seawater sample (5% of the original volume) and the addition of ammonia to reprecipitate the sample. The cleaned centrifuge tubes were capable of low iron and zinc blanks; however, we observed that samples left in the tubes but not processed immediately (e.g. left for greater than one week) and tubes reused after acid washing both produced spurious results.

*2.4 Inductively Coupled Plasma Mass Spectrometry*

A Thermo-Finnigan Element 2 (E2) inductively coupled plasma mass spectrometer (ICP-MS) was utilized for all analyses (see Table 1 for operating parameters). The E2 is a magnetic sector, high-resolution instrument capable of resolving transition elements from potentially interfering species. Isobaric interferences of $^{40}Ar^{16}O$ and $^{40}Ca^{16}O$ for $^{56}Fe$ and $^{15}N^{40}Ar$ for $^{55}Mn$ were easily resolved in medium resolution mode (R = 4000). The ~10-fold decrease in sensitivity associated with medium resolution versus low resolution detection was mostly offset by using an Aridus (Cetac Technologies) desolvating sample introduction system in conjunction with a low-flow PFA-Teflon nebulizer (Elemental Scientific Inc.) and an ASX-100 autosampler (Cetac Technologies). The Aridus greatly reduces oxide formation and gives a sensitivity boost of 5-10 times over a double-pass quartz spray chamber. Both standard and X skimmer cones (Spectron Inc.) were used in these measurements and the instrument was tuned each day for maximum signal intensity on $^{115}In$. X-cones have a unique geometry that improves sensitivity relative to standard cones.

*2.5 Calculation of Fe and Mn concentrations*

To minimize contamination, all samples were poured rather than pipetted into tubes in a clean room environment. Exact sample volume was determined by measuring weights of seawater added and converting to volume using the density of seawater. The concentration of the $^{57}Fe$ spike was calculated for the exact volume of each sample. Fe concentrations were calculated using a standard isotope dilution equation [30], following a correction for day-to-day variability in the instrument blank. Mn concentrations were determined by normalization to $^{57}Fe$ counts to correct for variability in $Mg(OH)_2$ recovery, followed by multiplying by the concentration of $^{57}Fe$ added to the initial 13mL sample, correcting for differences in instrument sensitivity between Mn and Fe, correcting for the contribution of $^{57}Fe$ from natural sources, and assuming that Mn had a high (near complete, 95%) scavenging efficiency as determined by the experiments described below.

*2.6 Experimental designs*

*Volume-Precision experiments*

Triplicate acidified seawater samples from the Equatorial Pacific (KM0405, 10° 79' N, 158° W, Station 4, 125m) were used for each volume tested (3mL, 5mL, 10mL, 13mL). Each sample was spiked to achieve an equivalent concentration of $^{57}Fe$ throughout the volume range. After overnight equilibration with the spike solution, all 12 tubes were precipitated with 160µl of concentrated ammonia and redissolved in 450µl of 5% nitric acid. The volume of ammonia added was kept uniform throughout the sample set as a precaution against varying blank load from that particular reagent. Due to the resultant larger precipitates in the 3mL and 5mL samples, those samples were further diluted to 800µl final volume with 5% nitric acid to avoid the possibility of instrumental problems due to high Mg load. The data is presented without blank correction to show how larger sample volumes can overcome difficulties with the instrumental blank.

*Successive Precipitations*

Recovery of trace elements during the precipitation process was examined by successively precipitating and redissolving a $Mg(OH)_2$ pellet. The losses associated with each precipitation should be observed with each precipitation iteration (e.g. three successive precipitations with 50% recovery should yield an overall recovery of 12.5%). Two experiments were performed, with and without $^{57}Fe$ spiked seawater for successive precipitations, using a batch of 500m seawater from the North Pacific (KM0311, 46° 57' N 170° 30' W, Stn 4). The first experiment had an initial precipitation of 13mL of sample, followed by repetitions of dissolving of the pellet in 50µl of 5% nitric acid, adding 0.65mL of seawater, and adding a small volume of ammonia for reprecipitation. The second experiment was the same as the first except for utilizing seawater spiked with $^{57}Fe$, as the initial experiment showed increasing ratios of M:$^{57}Fe$ as the $^{57}Fe$ tracer was diluted by the 5% additional volume (see below for results).

*Recovery Efficiencies Based on Standard Additions*

Three treatments were prepared in triplicate to examine the recovery efficiencies using standard additions: 1) standard additions to 5% nitric acid (control), 2) standard additions to samples prior to precipitation (to examine precipitation recovery), and 3) standard additions to samples after precipitation (to examine matrix effect). These standard additions were carried out using a combined stock solution of Fe, Mn and Co into 500m North Pacific seawater (KM0311, 46° 57' N 170° 30' W, Stn 4).

*Precipitation Time*

An experiment was conducted to examine the influence of precipitation time on trace element yields. Replicate samples of filtered and acidified Central Pacific seawater (KM0405, 10° 79’ N, 158° W Station 4, 125m) were precipitated with 160µL of concentrated ammonia for 3 to 40 minutes. The pellets were resuspended in 450µL of 5% nitric acid.

*Precipitation on Previously Precipitated Samples*

To test the efficiency of trace element preconcentration from seawater, the decanted seawater from precipitated samples was reprecipitated to determine the residual trace element concentrations. Because the ammonia added only removes a fraction of the magnesium from seawater, precipitating additional $Mg(OH)_2$ is straightforward. An experiment was conducted where 7.0mL of filtered Central Pacific seawater that was previously precipitated as described above (KM0405, 10° 79' N, 158° W, Station 4, 100m) was decanted into fresh tubes, centrifuged again to avoid carry over of precipitate, and the supernatant was then pipetted into new clean tubes. A proportional amount of $^{57}Fe$, as used in the original precipitation reaction, was then added to this seawater. The seawater was precipitated again and prepared for analysis as described above.

*Exposure of Precipitates to New Samples*

It has been unclear whether it is during the formation of the $Mg(OH)_2$ precipitate that trace elements are incorporated from seawater, or whether trace elements are effectively scavenged by adsorption onto the surface area of these precipitates after crystal formation. To try to differentiate between these possibilities, triplicate previously precipitated $Mg(OH)_2$ pellets were resuspended in fresh samples from Central Pacific seawater (KM0405, 10° 79' N, 158° W, Station 4, 125m) and additional $^{57}Fe$ tracer was added (equivalent to the amount used to make the original pellets). Results are reported both as counts per second (cps) and cps normalized to $^{57}Fe$.

*2.7 Vertical Profile from the Equatorial Pacific and Certified Reference Materials*

A vertical profile from the Equatorial Pacific south of Hawaii (KM0405 Station 7 at 12° 42.35' N, 158° W, Saito Chief-Scientist) was analyzed in duplicate using the double precipitation protocol presented in this manuscript. Concentrations of Fe and Mn are referred to as "dissolved" (as opposed to particulate) by operational definition of filtration through an acid cleaned 0.4μm polycarbonate filter, with subsequent acidification to pH 1.7 until analysis as described above.

Reference seawater from the National Research Council of Canada (NRCC, open ocean seawater standard NASS-5) was used to verify the accuracy of this method for Mn and Fe.

## 3. Results and Discussion

The Mg precipitation method has the potential to become a high-throughput method with excellent precision for the analysis of multiple trace elements. In this manuscript, we explore some of the important nuances of trace element preconcentration that occur during the precipitation reaction. These results will contribute to the adaptation of this method to additional metals, in particular those without multiple stable isotopes such as manganese ([29] and this manuscript) and cobalt (future studies).

In order to probe the $Mg(OH)_2$ precipitation chemical reaction, experiments were run that manipulated 1) seawater volume, 2) precipitation time, 3) the number of successive precipitations, 4) precipitation of previously precipitated seawater, and 5) exposure of precipitates to fresh seawater. In addition, recovery experiments were conducted using additions of Fe, Mn, and Co to 1) seawater samples, 2) a previously precipitated $Mg(OH)_2$ -nitric acid matrix, and 3) 5% nitric acid solutions.

### *3.1 The influence of sample volume on precision and signal:blank*

In adapting the $Mg(OH)_2$ method for the Thermo Finnigan Element 2 (E2), Aridus desolvator, and autosampler, we initially utilized the 1.3mL volumes as described by Wu and Boyle [15], but progressed to larger volumes to improve the signal strength on the E2 and to allow the use of the autosampler by having a larger final volume (0.5mL here, versus 0.1mL). Wu and Boyle have previously discussed the use of larger sample sizes and their influence on signal strength and precision, but their pioneering work has thus far relied on 1.3mL volumes with excellent success [25]. Figure 1 shows the M:$^{57}$Fe ratios achieved from a range of sample volumes (3mL – 13mL) with each volume in triplicate. With increasing sample volume the M:$^{57}$Fe ratios decreased and precision was improved, with the triplicate 13mL sample volume having overlapping sample points. It should be pointed out that all samples were precipitated with equal amounts of ammonia to avoid any differences in reagent blanks, and as a result it was necessary to dilute the

3mL and 5mL samples by an additional 350µL to compensate for the higher $Mg(OH)_2$ precipitate. Hence the lower precision of the lower volumes is likely associated with three factors: 1) lower signal from the smaller sample sizes, 2) higher $Mg(OH)_2$ background/matrix effects, 3) dilution effects in the smaller volume samples. It is likely that the first of these three possibilities (lower signal due to sample size) is the dominant cause of the lower precision based on the low signals measured. This is particularly evident for cobalt, which has a much smaller signal relative to Fe and Mn and shows much lower precision at the smaller seawater sample volumes. Consistent with this interpretation, phosphorus ($^{31}P$:$^{57}Fe$) and manganese ($^{55}Mn$:$^{57}Fe$) both have strong signals throughout the sample size range and hence only show modest increases in precision with increasing sample volume. The decrease in the M:$^{57}Fe$ ratios with increasing volume is attributable to increases in sample signal relative to instrument and reagent blanks (these results were not blank corrected in order to demonstrate this effect here). As sample signal becomes significantly higher than the blank (~10x), the M:$^{57}Fe$ asymptotically approaches a horizontal line. The amplitude of this change matches that of the signal:blank ratios with Co and Fe showing a clear decrease in M:$^{57}Fe$, while Mn and P, with their very small blanks relative to signal, show little to no change.

*3.2 Successive precipitations*

In order to examine the element-specific recovery efficiency during the $Mg(OH)_2$ scavenging reaction (scavenging efficiency from hereon), seawater samples were precipitated and redissolved in a small amount of 5% nitric acid. Then 5% of the original seawater volume was added, and the sample was reprecipitated. Two experiments were conducted, one in which $^{57}Fe$ was omitted from the subsequent seawater additions (Figure 2), and one using subsequent seawater additions from $^{57}Fe$ spiked seawater (Figure 3, see later paragraph for discussion). The hypothesis being tested in this experiment is that elements with lower recovery efficiencies than $^{57}Fe$ itself should have noticeably decreasing M:$^{57}Fe$ ratios with successive precipitations.

In the first experiment, relatively high scavenging efficiencies were observed, causing the minor effect of the small unspiked seawater additions needed for successive precipitations to be noticeable. Because these 5% seawater additions (by volume of

original sample) did not contain $^{57}$Fe, the ratios of $^{56}$Fe: $^{57}$Fe, $^{55}$Mn: $^{57}$Fe and $^{31}$P: $^{57}$Fe were all observed to increase slightly with successive precipitations, rather than decrease as expected for elements believed to have low scavenging efficiency (cobalt concentrations in this experiment were below detection limits). These increases in the M: $^{57}$Fe appear to be caused by a slight dilution of the $^{57}$Fe signal relative to the $^{55}$Mn, $^{56}$Fe, and $^{31}$P (by addition of a seawater aliquot *without* $^{57}$Fe added), as well as a slight differential in scavenging efficiency between Fe, Mn, and P, and can be described by equations 1-4 (cps = counts per second as measured by ICP-MS, SE = scavenging efficiency, the 1.05 value corrects for the increase in $^{56}$Fe added by 5% seawater additions, and the 1.0 value reflects the lack of additional $^{57}$Fe spike):

$$\frac{^{56}\mathrm{Fe}}{^{57}\mathrm{Fe}} = \frac{cps_{(^{56}Fe)}}{cps_{(^{57}Fe)}} \tag{1}$$

$$\frac{^{55}\mathrm{Mn}}{^{57}\mathrm{Fe}} = \frac{cps_{(^{55}Mn)}}{cps_{(^{57}Fe)}} \tag{2}$$

$$(^{56}Fe{:}^{57}Fe)_{(2ndppt)} = \frac{1.05 \cdot ^{56}Fe_{(1stppt)} \cdot SE_{Fe}}{1.0 \cdot ^{57}Fe_{(1stppt)} \cdot SE_{Fe}} \tag{3}$$

$$(^{55}Mn{:}^{57}Fe)_{(2ndppt)} = \frac{1.05 \cdot ^{55}Mn_{(1stppt)} \cdot SE_{Mn}}{1.0 \cdot ^{57}Fe_{(1stppt)} \cdot SE_{Fe}} \tag{4}$$

SE for $^{56}$Fe and $^{57}$Fe should be the same and hence equation (3) cancels to $1.05(^{56}\mathrm{Fe}{:}^{57}\mathrm{Fe}_{(1stppt)})$, and equation (4) reduces to the effect of the $^{57}$Fe dilution times the ratio of Mn to Fe scavenging efficiencies $(1.0(^{56}\mathrm{Fe}{:}^{57}\mathrm{Fe}_{(1stppt)})(SE_{Mn}/SE_{Fe}))$. Figure 2 suggests that the scavenging efficiency of Mn is very slightly greater than that of Fe. This subtle differential between Fe and Mn scavenging efficiencies is contrary to what was expected: a decreasing ratio was expected based on very high recovery efficiency for Fe and a presumably lower one for Mn. However, in this experiment the $^{55}$Mn:$^{57}$Fe and

$^{31}P$:$^{57}Fe$ ratios increase slightly higher than the predicted 5% amount expected from $^{57}Fe$ dilution with unspiked seawater aliquots, whereas the $^{56}Fe$:$^{57}Fe$ increases at ~5% for the first two points and then deviates to a slightly higher value for the subsequent precipitations. The experimental variability relative to the modeled 5% line may be due to losses of $Mg(OH)_2$ precipitate in each reaction, and the associated loss in M:$^{57}Fe$ signal relative to the background $^{56}Fe$ blank. While experimental error makes it difficult to be quantitative about the scavenging in this experiment, we can conclude qualitatively that Mn and P scavenging efficiencies are equal to or greater than that of iron, by comparison of slopes.

The second experiment was designed to avoid the competing effects of dilution of the $^{57}Fe$ signal and the influence of scavenging efficiencies. The addition of $^{57}Fe$ to the aliquot of seawater used for successive precipitations avoided the added complexity caused by the ~5% increases in M (Mn, Fe, P) relative to $^{57}Fe$, as described above. Hence, in this experiment, the expected result if scavenging efficiency was 100% would be a horizontal line through each successive precipitation. The results of this experiment are consistent with the previous experiment where the $^{55}Mn$:$^{57}Fe$ values decrease only slightly (Figure 3), suggestive of a high scavenging efficiency for Mn (5.7% and 3.7% decrease in ratios in between the first and second, and second and third re-precipitations, respectively). In addition P and Fe both have high scavenging efficiencies as expected ($^{56}Fe$:$^{57}Fe$ decreased 9.1% and 1.1% in the second and third precipitations). In this experiment, there was sufficient cobalt signal to include it in the analysis. Interestingly, the $^{59}Co$: $^{57}Fe$ ratios decrease significantly with successive precipitations (22% and 15% in the second and third precipitations) suggesting that the scavenging efficiency of cobalt is significantly lower than that of Fe, Mn, and P. This second precipitation experiment with spiked seawater confirmed the results of the first experiment that Fe and Mn have high scavenging efficiencies. Moreoever, cobalt scavenging was observed to be significantly lower than that of Fe and Mn.

This second experiment with spiked seawater can also be quantitatively described by the same equations used above, but with a 1.05 value reflecting the expected increase in $^{57}Fe$ with the spiked seawater:

$$(^{56}Fe{:}^{57}Fe)_{(2ndppt)} = \frac{1.05 \cdot ^{56}Fe_{(1stppt)} \cdot SE_{Fe}}{1.05 \cdot ^{57}Fe_{(1stppt)} \cdot SE_{Fe}} \quad (5)$$

$$(^{55}Mn{:}^{57}Fe)_{(2ndppt)} = \frac{1.05 \cdot ^{55}Mn_{(1stppt)} \cdot SE_{Mn}}{1.05 \cdot ^{57}Fe_{(1stppt)} \cdot SE_{Fe}} \quad (6)$$

where the second precipitation should now have the equivalent $^{56}Fe{:}^{57}Fe$ ratio (equation (5) should now reduce to $^{56}Fe{:}^{57}Fe_{(1stppt)} * 1$) and the $^{55}Mn{:}^{57}Fe$ ratio should be reflective of the differences in scavenging efficiency between the two elements (equation (6) reduces to be $^{56}Fe{:}^{57}Fe_{(1stppt)} * SE_{Mn}/SE_{Fe}$). As with the previous experiment, this experiment demonstrates that the scavenging efficiency of Mn is quite high, very close to that of Fe. As with the previous experiment, the experimental error appears to be close to the magnitude of subtle differences $SE_{Fe}$ and $SE_{Mn}$, although this particular experiment suggests that $SE_{Fe}$ is greater than $SE_{Mn}$. $SE_{Co}$ is significantly lower than that of Fe and Mn, and suggests that a reproducible value for $SE_{Co}$ will need to be determined for accurate analysis and/or the preconcentration chemistry altered to increase the $SE_{Co}$. Further discussion of the potential of cobalt analyses using this method is provided in section 3.4.

*3.3 Analysis of Recovery Efficiencies Based on Standard Additions*

A more direct approach for examining the recovery efficiency was also undertaken by preparing samples with additions of a mixed standard solution. Two sets of control treatments were prepared: standard additions (using a mixed Fe, Co, and Mn standard solution) were added to 5% nitric acid solutions and to replicate dissolved $Mg(OH)_2$ matricies (see Materials and Methods for experimental details). The experimental treatment consisted of standard additions to seawater prior to precipitation. The results are presented as counts per second versus standard additions in Figure 4 (panels A,B,and D), and as ratios ($M{:}^{57}Fe$) in Figure 4 (panels C and E) and Table 2. These three conditions (additions to 5% nitric acid, additions to samples, and additions to matrix) were chosen to elucidate the differences between recovery/scavenging efficiencies and matrix effects for each element (Fe, Mn, and Co). In the additions to 5%

nitric acid, the sensitivities (slopes) for Fe, Mn and Co are quite similar (Figure 4A; Mn = 158000 cps/ppb, Fe = 149000 cps/ppb, Co = 145000 cps/ppb). When equivalent concentrations of these metals are added to seawater samples and concentrated using Mg precipitation the slopes were significantly lower than in nitric acid. Moreover, while Fe and Mn have slopes similar to each other, the slope of the cobalt standard additions was three-fold less (Figure 4B and 4C: Mn = 60200, Fe = 51000, Co = 18700). To differentiate between matrix effects and recovery efficiencies, standard additions to the $Mg(OH)_2$ matrix added post-precipitation are presented in panel C, and show similar slopes for the three elements relative to each other. There is some variability in the slopes in this matrix experiment because each sample likely had slightly different amounts of $Mg(OH)_2$ precipitate resulting in varying matrix effects. However, normalizing to the $^{57}Fe$ spike solution corrects for this variability to a large extent (Figure 4E). Together these results imply that while significant loss of sensitivity due to matrix effects is occurring (by comparison of panel A with that of D and E), there is also an additional recovery efficiency effect occurring, particularly for cobalt, which has a significantly lower slope in Figure 4B/C than 4D/E. Differences between Fe and Mn slopes are slight, showing if anything a slightly higher recovery efficiency for Mn than Fe in these experiments. These results are consistent with those in the successive precipitation experiments described above showing a high scavenging efficiency for Fe and Mn, and a significantly lower one for Co.

*3.4 Implications of Recovery Efficiency for Co Analyses using Mg Co-precipitation*

The loss in sensitivity due to matrix effects described above is corrected for by the $^{57}Fe$ spike, and hence is not detrimental to the method - it is in fact a necessary 'evil' of this co-precipitation method. However, the poor scavenging efficiency of cobalt, relative to that of Fe and Mn, is problematic for the application of this method to cobalt measurements using this method. Early studies of recovery of cobalt in gallium hydroxide induced magnesium precipitation in seawater demonstrated near complete recoveries [27], suggesting that this problem is not intractable, and is likely due to the specific protocol used here. In particular, it may be the small amounts of ammonia and resulting small precipitates used here compared to large sample and reactant volumes

used in the earlier Akagi et al. study that cause the observed differences in cobalt scavenging. The focus of this study was primarily on developing confidence in the manganese measurements; future studies should focus on modifying the protocol towards inclusion of additional elements, in particular cobalt, which recent studies have shown has a dynamic and intriguing biogeochemistry in marine environments [17, 31-35]. Our initial observations suggest that natural cobalt containing organic complexes and the cobalt containing biomolecule cobalamin (vitamin $B_{12}$) do not appear to be measured by this ICP-MS method and perhaps also by the other ICP-MS affinity column methods (Saito, unpublished data). In contrast, the electrochemical Co method utilizes a UV-irradiation step that we have observed to liberate cobalt from both types of cobalt-organic complexes quite effectively and rapidly (Saito and Noble, in preparation). Hence, these ICP-MS methods may seriously underestimate the abundance of cobalt in seawater relative to electrochemical methods. However, we believe that both of these problems are solvable, and that future studies should be able to produce a high-throughput oceanic seawater cobalt ICP-MS method.

*3.5 Influence of Precipitation Time on Recovery Efficiency*

Previous studies have discussed the potential importance of precipitation time on controlling the amount of precipitate as well as its possible influence on recovery efficiencies of Mn. Given the larger sample volumes used in this modified protocol, very short precipitation times did not seem practical. Furthermore, the high precision of analyses observed using this protocol suggested that there was not an inherent variability associated with precipitation times that was negatively affecting precision. As a result experiments were conducted to examine the influence of a range of precipitation times from 3 to 40min (Figure 5). Little variability was observed for the first three timepoints (3, 10, 15min) in this experiment for Mn and Fe (panel A.), after which some variability was observed perhaps due to error associated with increased matrix effects of the larger concentration of Mg in the final samples. Zn, Co, and Cu were also examined for their M:$^{57}$Fe variability with longer precipitation times (panels B and C). Co was similar to Fe and Mn in showing little variability with time. However, Zn decreased in signal strength with time and Cu increased in signal strength with time. Presumably Cu scavenging was

not complete within the initial few minutes as appears to be the case for Mn, Fe, and Co, and suggests that once the precipitate is formed surface adsorption may occur for copper remaining in the dissolved form in the seawater sample. In contrast, Zn:$^{57}$Fe ratios decrease with time, which is a difficult result to explain. Perhaps Zn is adsorbed rapidly onto the $Mg(OH)_2$ particles and then back reacts with time and is redissolved in the seawater sample. While the case of Zn and Cu are surprising, these results likely do not have negative implications for the analytical potential of the $Mg(OH)_2$ precipitation method for these elements since both of Zn and Cu can be analyzed by isotope dilution and hence any variability in recovery efficiency should be corrected for by the use of the Zn and Cu isotopic spikes. It is fortuitous that Mn and Co are not observed to undergo variations in recovery with increasing time since both of these elements do not have multiple stable isotopes which could be used for isotope dilution.

*3.6 Precipitation on Previously Precipitated Sample*

As an additional examination of the recovery efficiency (pers. comm. S. John) decanted seawater from a precipitated sample was then re-precipitated with a new addition of ammonia (see Materials and Methods for details). Figure 6 shows the results of this experiment for Mn and P, where triplicate decanted solutions showed little additional Mn removal from the seawater, implying near complete removal during the first precipitation reaction. If this were not the case and the scavenging efficiency were lower (e.g. 50%) we might expect a subsequent ammonia addition to the supernatant to successfully scavenge a fraction of the residual elements in the supernatant (e.g. 50% of the original residual 50%, or 25% of the original signal). The results here are consistent with our previous experiments on scavenging efficiency of Mn suggesting near complete removal of Mn from the sample.

*3.7 Exposure of Precipitate to a New Sample*

An experiment was conducted to examine the ability of pre-formed $Mg(OH)_2$ crystals to scavenge metals from seawater. Precipitated $Mg(OH)_2$ was exposed to a fresh 13mL sample of seawater and shaken without additional ammonia. Figure 7 shows the results in terms of counts per second and normalized to $^{57}$Fe. Two sets of triplicate

samples were used: a control treatment where the precipitate was not exposed to a new sample, and an experimental treatment where the precipitate was exposed to a fresh sample. The ratios of Fe and Mn are only slightly higher with the additional exposure to fresh sample, suggesting that it is the precipitation reaction rather than surface adsorption that is the major mechanism of pre-concentration. However, phosphorus increases significantly with an additional scavenging reaction (Figure 8) demonstrating that it is concentrated via an adsorption reaction rather than by (or in addition to) incorporation into the $Mg(OH)_2$ precipitate. This effect of $Mg(OH)_2$ scavenging P is consistent with what has been observed previously in the development of the MAGIC P method [28].

*3.8 The Influence of Sample and Skimmer Cones on Sensitivity*

Both standard and X skimmer cones were tested for their sensitivity using standard solutions. In Table 3, the slopes of standard solutions of P, Mn, Fe, and Co for both types of cones demonstrate a 5.1 to 6 fold increase in sensitivity with X-cones relative to standard cones. While this improvement in sensitivity is appealing, we did not find it to be particularly advantageous for Fe and Mn because the instrument blank increased proportionally with sensitivity. However, for Co analyses this may be advantageous given the very low blank for Co on the E2 and since the Co signals tended to be very small due to the combination of low concentrations in seawater and poor scavenging efficiencies.

## 4. Applications of the modified $Mg(OH)_2$ precipitation protocol

*4.1 Analysis of NASS-5 Reference Seawater materials*

To verify accuracy, analyses were made on National Research Council of Canada (NRCC) open ocean seawater standard NASS-5. As presented in Table 4, the precision and accuracy were quite good on parallel quadruplicate samples, with relative standard deviations of 1.2% for Fe and 2.4% for Mn. It should be pointed out that even though this seawater is described as “open ocean”, the iron and manganese concentrations are very high relative to published reports of open ocean iron and manganese. Analyses of the SAFE intercomparison samples shows very good consistency between this method and reports from other established groups.

*4.2 Application of Method to an Equatorial Pacific Vertical Profile*

Example profiles of dissolved Fe and Mn are shown in Figure 9 near the equatorial Pacific at $12^{o}$ 42.35' N, $158^{o}$W. These particular samples were precipitated twice and centrifuged twice after each precipitation to remove all traces of seawater. Standard deviation of the duplicate sample analyses produced error bars for most depths that are smaller than the symbols. Further discussion of these profiles in an oceanographic context and with other profiles generated using this method will be presented elsewhere (Saito, in prep).

*4.3 Comments on Precision, Accuracy, and Future Efforts*

The precision of the ICP-MS method described here is extremely good, approximately 1.2 - 2.4% RSD. Multiple experiments designs demonstrated that the scavenging efficiency of Mn is near complete, similar to that of Fe. The accuracy was very sensitive to the measured concentration of the $^{57}$Fe spike solution and precautions should be taken when utilizing this method to regularly calibrate relative to known standard materials. Further refinement and quantification of the scavenging efficiency values could allow slight improvement in the method's accuracy for elements that cannot utilize isotope dilution such as Mn. Future efforts should include applying this promising method to additional trace elements.

**References**


[1] J.K. Moore, S.C. Doney and K. Lindsay, Global Biogeochem. Cycles 18 (2004) doi:10.1029/2004GB002220.

[2] K.S. Johnson, R.M. Gordon and K.H. Coale, Mar. Chem 57 (1997) 137-161.

[3] I.Y. Fung, S.K. Meyn, I. Tegen, S.C. Doney, J.G. John and J.K.B. Bishop, Global Biogeochem. Cycles 14 (2000) 281-291.

[4] K.W. Bruland, R.P. Franks, G.A. Knauer and J.H. Martin, Anal. Chim. Acta 105 (1979) 223-245.

[5] J.H. Martin and R.M. Gordon, Deep-Sea Res 35 (1988) 177-196.

[6] J.H. Martin, R.M. Gordon, S. Fitzwater and W.W. Broenkow, Deep-Sea Res. 36 (1989) 649-680.

[7] K.W. Bruland, Earth Planet. Sci. Lett. 47 (1980) 176-198.

[8] K.W. Bruland, K.H. Coale and L. Mart, Mar. Chem. 17 (1985) 285-300.

[9] A.R. Bowie, P.N. Sedwick and P.J. Worsfold, Limnol. Oceanogr. Methods 2 (2004) 42-54.

[10] V. Elrod, K.S. Johnson and K.H. Coale, Anal. Chem. 63 (1991) 893-898.

[11] C.M.G. van den Berg, Mar. Chem. 50 (1995) 139-157.

[12] E.L. Rue and K.W. Bruland, Mar. Chem. 50 (1995) 117-138.

[13] J. Wu and G. Luther, Mar. Chem. 50 (1995) 159-177.

[14] J. Wu and E.A. Boyle, Anal. Chem. 69 (1997) 2464-2470.

[15] J. Wu and E.A. Boyle, Anal. Chim. Acta 367 (1998) 183-191.

[16] C.I. Measures, J. Yuan and J.A. Resing, Mar. Chem. 50 (1995) 3-12.

[17] M.A. Saito and J.W. Moffett, Mar. Chem. 75 (2001) 49-68.

[18] K.W. Bruland, Limnol. Oceanogr. 37 (1992) 1008-1016.

[19] K.W. Bruland, Limnol. Oceanogr. 34 (1989) 269-285.

[20] C.M.G. van den Berg and M. Nimmo, Sci. Total Environ. 60 (1987) 185-195.

[21] M.P. Field, J.T. Cullen and R.M. Sherrell, J. Anal. At. Spectrom. 14 (1999) 1-7.

[22] M.C. Lohan, A.M. Aguilar-Islas, R.P. Franks and K.W. Bruland, Anal. Chim. Acta (2004).

[23] M. Kinugasa, T. Ishita, Y. Sohrin, K. Okamura, S. Takeda, J. Nishioka and A. Tsuda, Prog. Oceanogr. 64 (2005) 129-147.

[24] H. Obata, H. Karatani and E. Nakayama, Anal. Chem. 65 (1993) 1524-1528.

[25] J. Wu and E.A. Boyle, Global Biogeochem. Cycles 16 (2002) 331-337.

[26] GEOTRACES, http://www.ldeo.columbia.edu/res/pi/geotraces/.

[27] T. Akagi, K. Fuwa and H. Haraguchi, Anal. Chim. Acta 177 (1985) 139-151.

[28] D.M. Karl and G. Tien, Limnol. Oceanogr. 37 (1992) 105-116.

[29] E.A. Boyle, B.A. Bergquist, R.A. Kayser and N. Mahowald, Geochim. Cosmo. Acta 69 (2005) 933-952.

[30] G. Faure, Principles of Isotope Geology, John Wiley & Sons, New York, 1986.

[31] M.A. Saito, J.W. Moffett and G. DiTullio, Global Biogeochem. Cycles 18 (2004) GB4030, doi:10.1029/2003GB002216.

[32] M.A. Saito, G. Rocap and J.W. Moffett, Limnol. Oceanogr. 50 (2005) 279-290.

[33] M.A. Saito and J.W. Moffett, Geochim. Cosmochim. Acta 66 (2002) 1943-1953.

[34] M.A. Saito, D. Sigman and F.M.M. Morel, Inorg. Chim. Acta 356 (2003) 308-318.

[35] M.J. Ellwood and C.M.G. van den Berg, Mar. Chem. 75 (2001) 33-47.

**Figure Captions**

Figure 1. The influence of the volume of seawater precipitated on the precision and signal-to-blank ratio. Previous studies have typically used 1.3mL volumes. Increases in precipitated volume greatly increase precision and asymptotically approach a "correct" ratio once the signal is sufficiently higher than the blank. The precision at the 3mL and 5mL volumes are somewhat exaggerated due to the need to dilute the samples by an additional 1.7 fold to reduce Mg interferences (see text). Blank corrections were purposely omitted to demonstrate the influence of sample volume on the blank.

Figure 2. Precipitation of previously precipitated seawater to examine recovery, without the use of $^{57}Fe$ spiked aliquots for successive precipitations (aliquots are 5% of original volume).

Figure 3. Precipitation of previously precipitated seawater to examine recovery, using $^{57}Fe$ spiked aliquots for successive precipitations (aliquots are 5% of original volume).

Figure 4. Analysis of Mn, Fe, and Co additions to A) 5% nitric acid, B) seawater samples (additions prior to precipitation), C) seawater samples (additions prior to precipitation) normalized to $^{57}Fe$, D) $Mg(OH)_2$ matrix redissolved in 5% nitric acid (additions after precipitation), and E) $Mg(OH)_2$ matrix redissolved in 5% nitric acid (additions after precipitation) normalized to $^{57}Fe$. While all three elements have similar ionization efficiencies (panel A), the scavenging efficiencies of Fe and Mn are significantly better than that of Co (panel B and C). Decreases in slope in panels B-E are caused by the $Mg(OH)_2$ matrix effects as well as the poor scavenging efficiency of cobalt. When normalized to $^{57}Fe$ significantly higher $r^2$ values are obtained relative to the counts per second values.

Figure 5. The effect of precipitation time on the scavenging of A) Mn, Fe, B) Zn, C) Co, and Cu. Longer scavenging times do not appear to increase the scavenging of all elements with the exception of Cu. Fe, Mn, and Co scavenging remains relatively

constant despite longer precipitation times. Zn appears to decrease relative to $^{57}Fe$, and Cu appears to increase with longer durations.

Figure 6. The seawater supernatant from precipitated samples was decanted and reprecipitated to examine if further Mn or P could be recovered. Solid bars indicate the $^{55}Mn$:$^{57}Fe$ and $^{31}P$:$^{57}Fe$ ratio of the initial sample, and grey bars indicate those ratios on 7mL of of the supernatant. Error bars reflect standard deviation of triplicate analyses. Negligible Mn is concentrated from the supernatant, and a small portion of P is concentrated.

Figure 7. $Mg(OH)_2$ precipitates were exposed to fresh seawater sample (without added $^{57}Fe$) to examine if the precipitate when resuspended could scavenge additional Fe or Mn. A) Fe and Mn presented in counts per second show no significant change when exposed to fresh seawater. B) Ratios relative to $^{57}Fe$ are presented, correcting for losses of $Mg(OH)_2$. Error bars reflect standard deviation of triplicate analyses. These data suggest that the initial precipitation reaction, rather than the exposure to the already formed $Mg(OH)_2$, is when the metal preconcentration occurs.

Figure 8. $Mg(OH)_2$ precipitates were exposed to fresh seawater sample (without added $^{57}Fe$) to examine if the precipitate when resuspended could scavenge additional P. $^{31}P$ presented in counts per second increases significantly when exposed to fresh seawater. Ratios relative to $^{57}Fe$ are presented, correcting for losses of $Mg(OH)_2$. These data indicate that unlike for Fe and Mn (see Figure 7), the $Mg(OH)_2$ precipitate is capable of scavenging P from seawater. Error bars reflect standard deviation of triplicate analyses.

Figure 9. Vertical profiles of A) iron and B) manganese in the Central Pacific south of the Hawaiian Islands (12° 42.35’ N, 158° W Station 7, KM0405) measured using the protocol described in this study.

**Acknowledgements**

The authors would like to thank Ed Boyle, Seth John, Bridget Bergquist, Rachel Wisneiwski, and Lary Ball for helpful discussions and Peter Sedwick and Tom Church for pointing us to early co-precipitation studies. We are indebted to Rachel Wisneiwski, Carl Lamborg, Ed Sholkovitz, Sheila Clifford and an anonymous reviewer for comments on this manuscript and to Tyler Goepfert and Gary Fones for assistance with sample collection. This research was supported by NSF grants OCE-0327225, OCE-0452883, and the Center for Environmental Bioinorganic Chemistry at Princeton.

Figure 1.

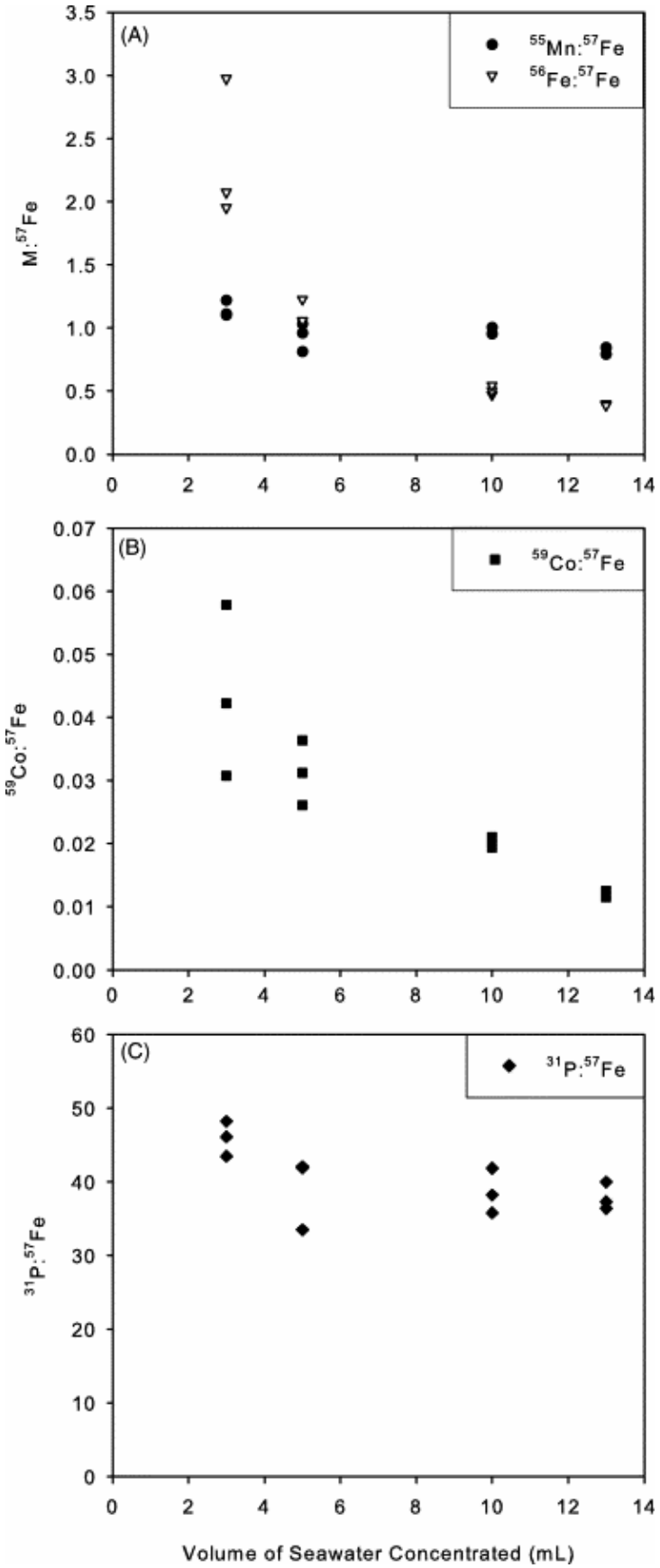

(A)
$^{55}Mn:^{57}Fe$
$^{56}Fe:^{57}Fe$
M:$^{57}$Fe
(B)
$^{59}Co:^{57}Fe$
$^{59}$Co:$^{57}$Fe
(C)
$^{31}P:^{57}Fe$
$^{31}$P:$^{57}$Fe
Volume of Seawater Concentrated (mL)

Figure 2.

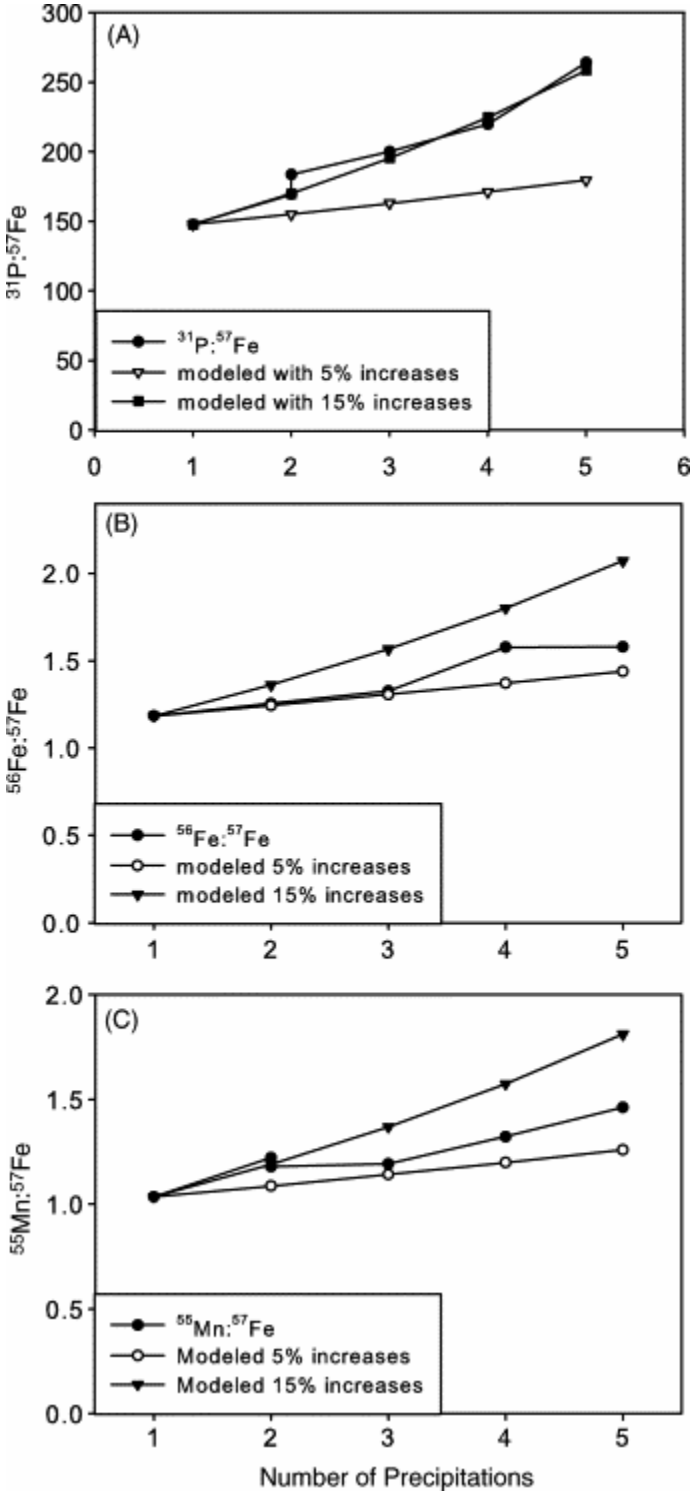

(A)
$^{31}P$:$^{57}Fe$
$^{31}P$:$^{57}Fe$
modeled with 5% increases
modeled with 15% increases
(B)
$^{56}Fe$:$^{57}Fe$
$^{56}Fe$:$^{57}Fe$
modeled 5% increases
modeled 15% increases
(C)
$^{55}Mn$:$^{57}Fe$
$^{55}Mn$:$^{57}Fe$
Modeled 5% increases
Modeled 15% increases
Number of Precipitations

Figure 3.

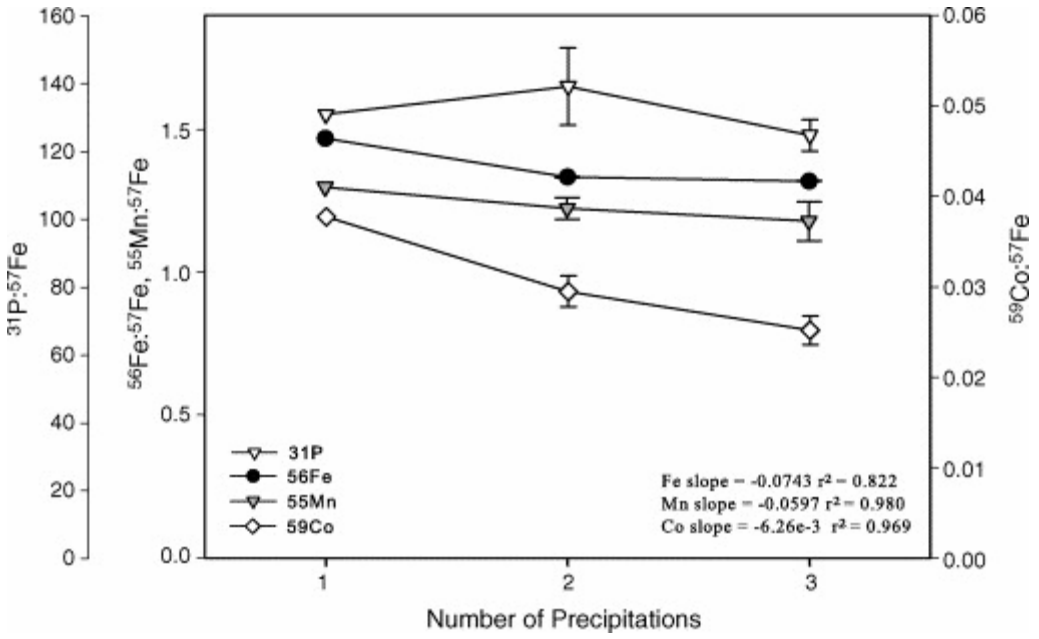

160
140
120
100
80
60
40
20
0
31P:57Fe
1.5
1.0
0.5
0.0
56Fe:57Fe, 55Mn:57Fe
0.06
0.05
0.04
0.03
0.02
0.01
0.00
59Co:57Fe
31P
56Fe
55Mn
59Co
Fe slope = -0.0743 r² = 0.822
Mn slope = -0.0597 r² = 0.980
Co slope = -6.26e-3 r² = 0.969
1
2
3
Number of Precipitations

Figure 4.

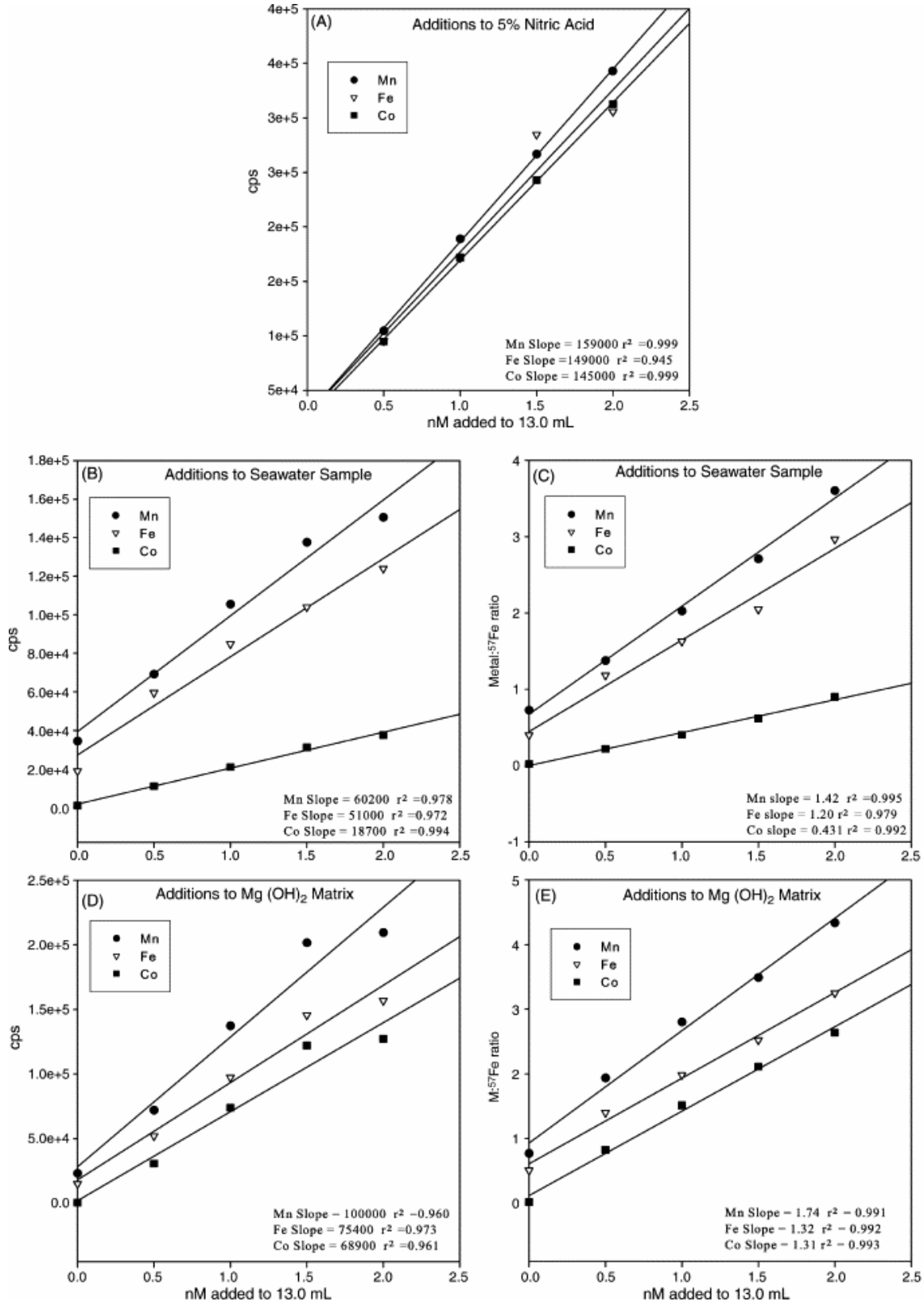

(A)
Additions to 5% Nitric Acid
Mn
Fe
Co
cps
Mn Slope = 159000 r² =0.999
Fe Slope =149000 r² =0.945
Co Slope = 145000 r² =0.999
nM added to 13.0 mL
(B)
Additions to Seawater Sample
Mn Slope = 60200 r² =0.978
Fe Slope = 51000 r² =0.972
Co Slope = 18700 r² =0.994
(C)
Additions to Seawater Sample
Metal:57Fe ratio
Mn slope = 1.42 r² =0.995
Fe slope = 1.20 r² = 0.979
Co slope = 0.431 r² = 0.992
(D)
Additions to Mg (OH)2 Matrix
Mn Slope = 100000 r² =0.960
Fe Slope = 75400 r² =0.973
Co Slope = 68900 r² =0.961
(E)
Additions to Mg (OH)2 Matrix
M:57Fe ratio
Mn Slope = 1.74 r² = 0.991
Fe Slope = 1.32 r² = 0.992
Co Slope = 1.31 r² = 0.993

Figure 5.

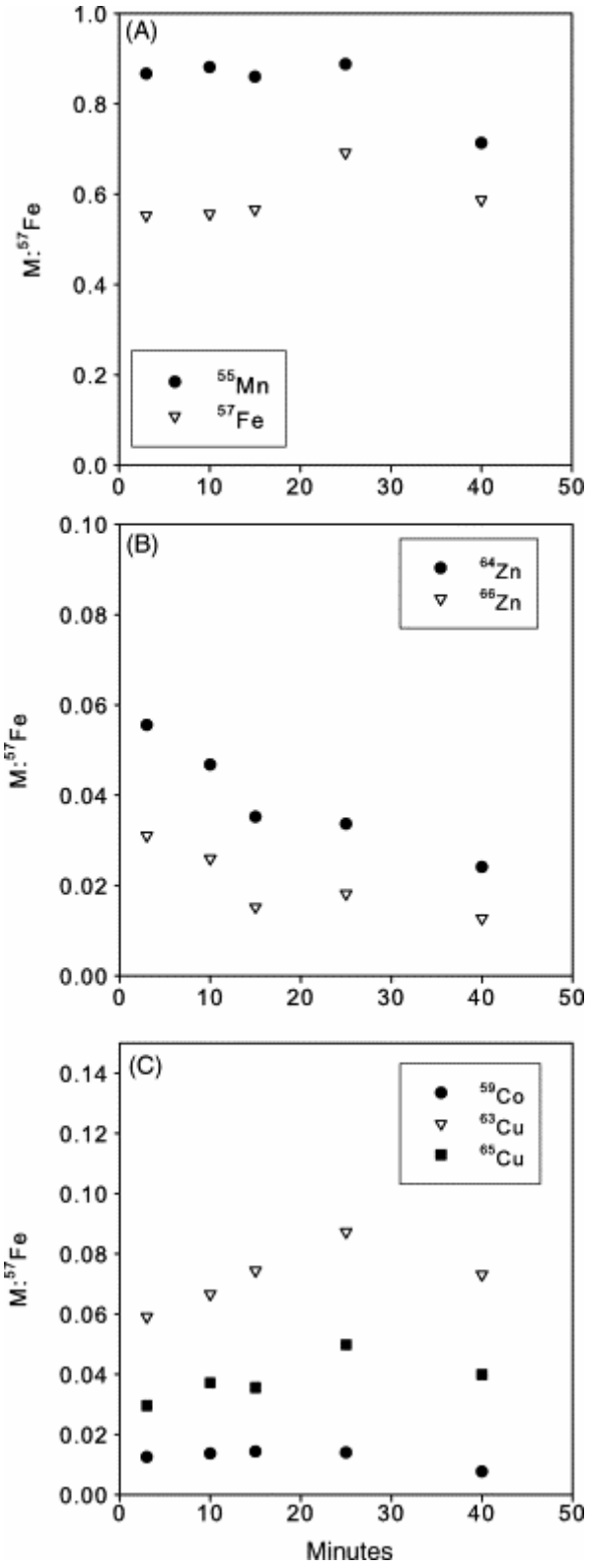


Figure 6.

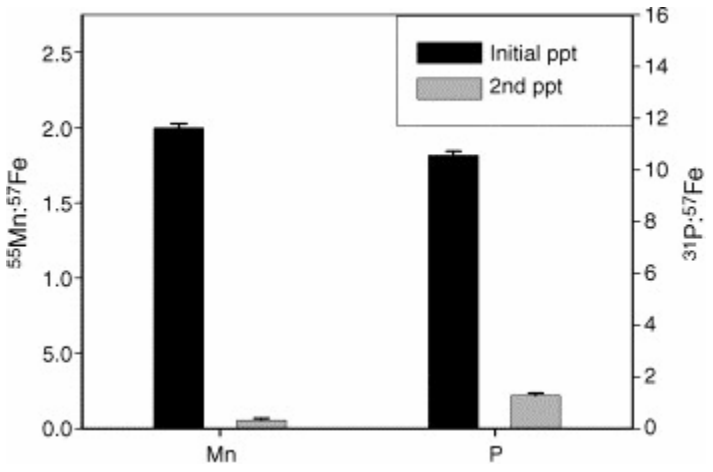

Initial ppt
2nd ppt
55Mn:57Fe
31P:57Fe
2.5
2.0
1.5
1.0
5.0
0.0
16
14
12
10
8
6
4
2
0
Mn
P

Figure 7.

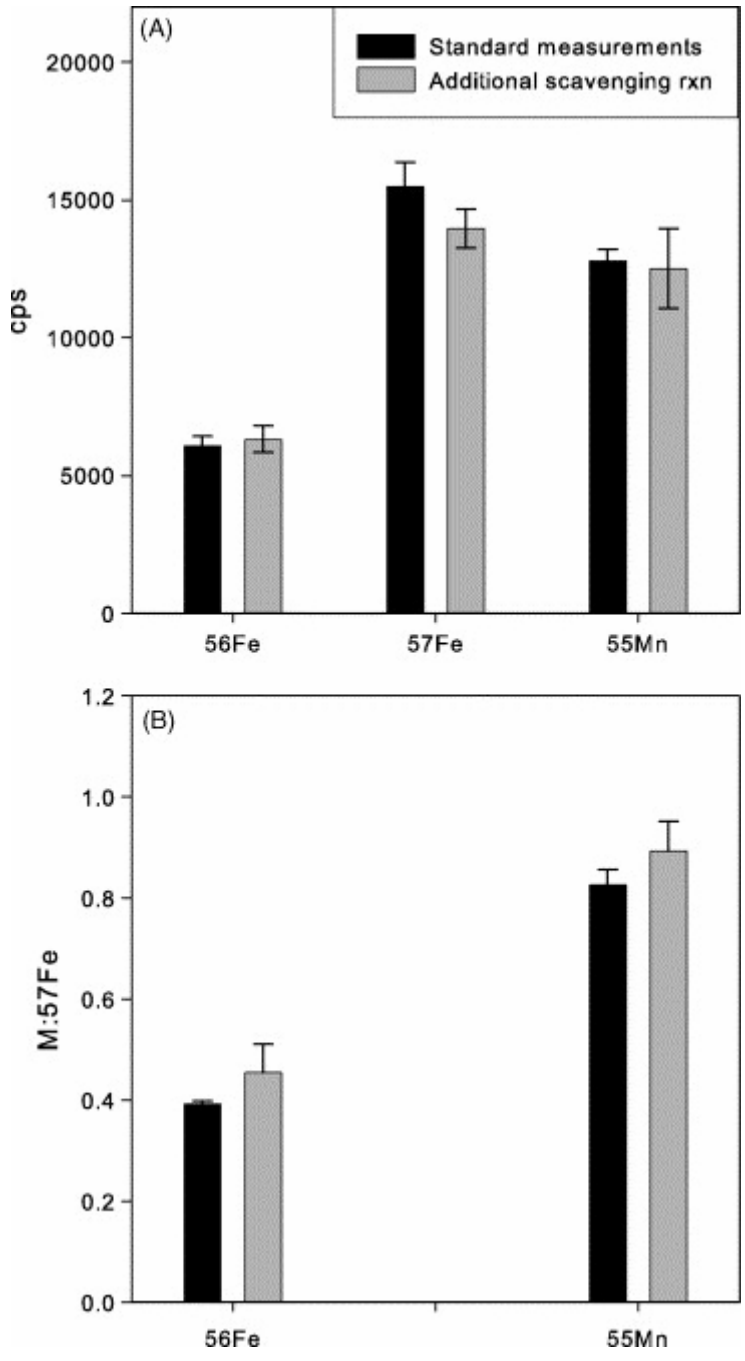

(A)
Standard measurements
Additional scavenging rxn
cps
20000
15000
10000
5000
0
56Fe
57Fe
55Mn
(B)
M:57Fe
1.2
1.0
0.8
0.6
0.4
0.2
0.0
56Fe
55Mn

Figure 8.

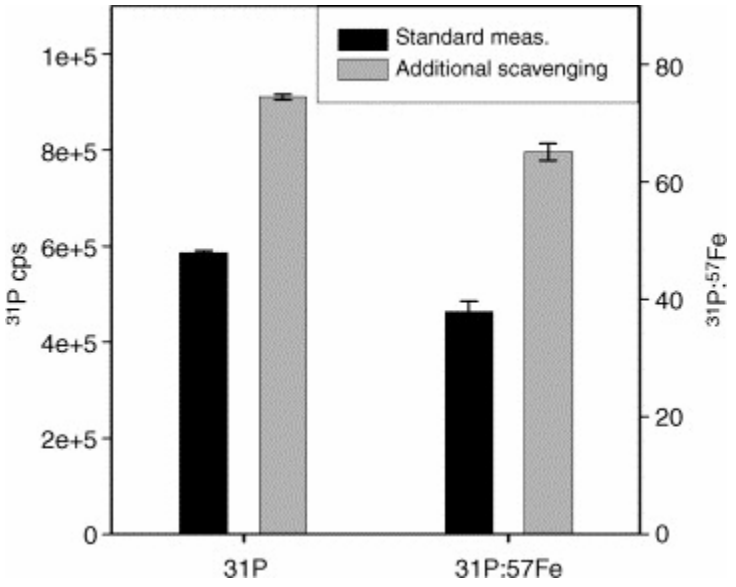
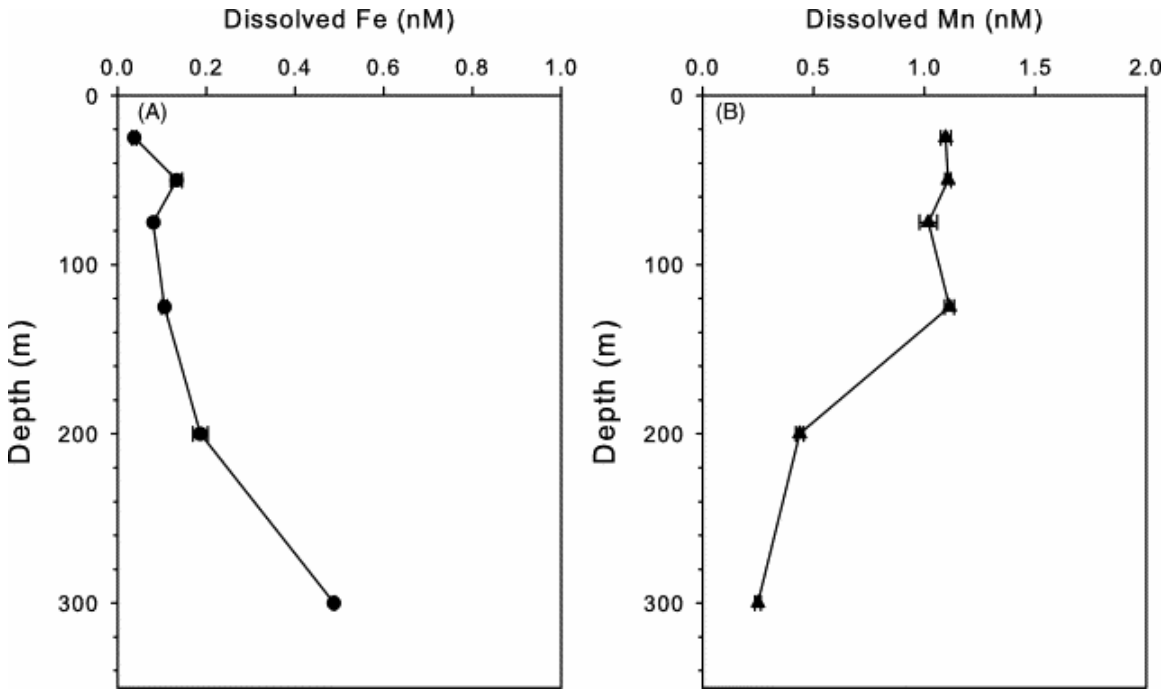

Standard meas.
Additional scavenging
1e+5
8e+5
6e+5
4e+5
2e+5
0
31P cps
80
60
40
20
0
31P:57Fe
31P
31P:57Fe

Figure 9.


Dissolved Fe (nM)
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
Depth (m)
(A)
Dissolved Mn (nM)
0.0
0.5
1.0
1.5
2.0
0
100
200
300
Depth (m)
(B)